

viewpoint of morphology control, it is necessary to prepare silica with different morphologies for shape control of mesoporous carbons, because carbon usually preserves the morphology of the silica.

Direct organic templating methods that eliminate the need for mesoporous silica scaffolds have recently been developed to synthesize highly ordered mesoporous carbons [6–16]. Dai et al. have prepared well-ordered mesoporous carbon films by means of a stepwise assembly approach using polystyrene-*block*-poly(4-vinylpyridine) [6]. As an alternative approach, our and Nishiyama's groups first used triblock copolymer Pluronic F127 as a soft template and performed spin coating to deposit ordered carbon films, designated COU-1 and CKU-F69, on various substrates [7,8,13]. This strategy uses an organic–organic interaction between a thermoplastic resin and a thermally-decomposable copolymer to form a periodic ordered nanocomposite. The thermoplastic resin remains as the carbonaceous pore walls, while Pluronic F127 decomposes to form the mesopores. The soft-templating approach has been developed by us and several other research groups over the last few years. Zhao et al. used mainly a phenol/formaldehyde as a carbon precursor and synthesized a variety of bulk mesoporous carbons with several unique structures including a two-dimensional hexagonal phase *p6mm*, a body-centered cubic phase *Im3m*, and a gyroid-based cubic phase *Im3d* [9–11].

Simple techniques to control morphology and configuration of mesoporous carbons are required for the development of practical applications. We note that the soft-templating approach is advantageous for controlling the morphology and configuration (film, powder, and fiber). However, as far as we can see, control of morphology and configuration still seems to be more difficult for mesoporous carbons than for mesoporous silicas. Further systematic understanding is required to synthesize ordered mesoporous carbon materials.

Here, we report a simple synthesis of mesoporous carbons in film, powder, and fiber morphologies by means of organic–organic self-assembly using two different types of phenolic resin monomers: resorcinol (Res) and phloroglucinol (Phl), and Pluronic F127. Completely continuous films composed of ordered mesoporous carbon were obtained by dip-coating a silicon substrate. Ordered mesoporous carbon powders were obtained by the sol–gel method with adjustments of the EtOH/water molar ratio. Mesoporous carbon nanofibers were prepared within the channels of anodic aluminum oxide (AAO) membranes followed by dissolution of the membrane. The porous structure has been studied with a different morphology of mesoporous carbons prepared from the same precursor solution.

2. Experimental

2.1. Chemicals

Resorcinol, phloroglucinol, formaldehyde (36–38 wt%), 5 N HCl, and ethanol were purchased from Wako Pure Chemical Industries and used as received. Pluronic F127 was purchased from Sigma–Aldrich Chemical Co. and used as received.

2.2. Synthesis of mesoporous carbon films

Resorcinol and phloroglucinol were completely dissolved in EtOH/water solution, HCl was added, and the solution was stirred for 30 min. Pluronic F127 was then added, and after it was completely dissolved, formaldehyde was added. The final molar composition of the coating solution was 3 resorcinol:1 phloroglucinol:0.02 Pluronic F127:9 formaldehyde:0.1 HCl:20–100 ethanol:40 water. Thin films were prepared by evaporation-induced self-assembly via dip-coating the silicon substrates in the coating solutions at a withdrawal rate of 1.2 mm/s using a DIPCOATER DC4200 (Aiden Co., Ltd.). For polymerization of the resorcinol and phloroglucinol with formaldehyde, the as-deposited samples were pre-heated at 100 °C for 1 h in air. The resultant brown deposition was carbonized under a nitrogen atmosphere at 200–800 °C for 3 h at a heating rate of 1 °C/min.

2.3. Synthesis of mesoporous carbon powders

The preparation of precursor solutions was as described above. The solutions were left for 3 days at room temperature, during which they separated into two phases. The upper clear phase was discarded; the lower dark brown phases were pre-heated at 100 °C for 1 h in air. The subsequent carbonization process was performed according to the above procedure.

2.4. Synthesis of mesoporous carbon nanofibers

AAO membranes (average pore diameter = 200 nm, thickness = 60 µm, membrane diameter = 25 mm) were obtained from Whatman (Anodisk). The membrane was set in an ordinary membrane filtration apparatus, and the precursor solution described above was dropped onto it. Moderate aspiration was applied so that the solution penetrated into the columnar alumina pores. The membrane including the precursor solution was dried in air at 100 °C for 1 h. Carbonization was performed as described above. The AAO scaffold was completely removed by immersing the composite membrane in 5 M NaOH solution at 100 °C for 24 h.

2.5. Characterization

The ordered structure of the samples was investigated with powder X-ray diffraction (PXRD) and small-angle X-ray scattering (SAXS). PXRD patterns were recorded on a RINT-TTR III diffractometer (Rigaku Co.) using Cu K α radiation; the copper anode was operated at 40 kV and 20 mA. SAXS measurements were recorded on a MXP-SAXS3 MO3XHF (Mac Science Co., Ltd.) using Cu K α radiation with $\lambda = 1.5418$ Å; the copper anode was operated at 40 kV and 30 mA.

Two dimensional grazing-incidence small-angle X-ray scattering (GISAXS) was used to determine the symmetry, order, and orientation of the films. Because of the presence of an intense specular beam at grazing angles of incidence, aluminum strips were used to attenuate scattering along the specular plane. The GISAXS patterns were analyzed using a Mathematica-based program called NANOCCELL.